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ORIGINAL ARTICLE

Magnetic entropy change in bulk nanocrystalline Gd metals

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Abstract The magnetocaloric properties of the as-consolidated nanocrystalline and coarse-grained gadolinium metals were studied in the present work. With the decrease of Gd grains from micrometer to nanometer range, magnetic entropy change drops surprising from 10.07 to 4.47 J kg^{-1} K^{-1} at a magnetic-field change of 5 T, and their resultant magnetic entropy change uniformly peaks at 294, 290, and 288 K, respectively, corresponding to the magnetic transition temperature of the three samples. The Curie temperature T_C of the nanocrystalline Gd shifts by more than 6 K below that of coarse-grained Gd sample. However, the values of magnetic entropy change of the nanocrystalline metals exhibit a more constant tendency compared with the coarse-grained sample. The Arrott plots indicate the second-order character of magnetic phase transition still in the nanocrystalline Gd metals. The refrigerant capacity calculated is also used to evaluate material refrigeration capacity.

Keywords Magnetocaloric effect · Magnetic entropy changes (ΔS) · Nanocrystalline metals

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Introduction

In recent years, magnetic refrigeration technology has attracted extensive attention due to its good energy efficiency, small volume and environment amity, when compared with the conventional gas-compression cooling (Pecharsky and Gschneidner 1999; Pecharsky et al. 2005). As a result, many magnetic materials with large magnetocaloric effect (MCE) have been developed and comprehensively investigated for the moment.

Recently, the research and development efforts in the area of magnetic refrigeration have been concentrated in the nanoscale magnetic materials due to a large MCE in the nanostructured materials (McMichael et al. 1992, 1993; Bennett et al. 1994; Shao et al. 1996). Considerable investigations indicate that the nanostructured materials are very promising candidates for potential application in the magnetic refrigeration (Zhang et al. 2001; Tanaka et al. 2001; Hueso et al. 2002; Provenzanoa et al. 2003; Shir et al. 2003; Kinoshita et al. 2004; Evangelisti et al. 2005; Poddar et al. 2006; Gómez-Polo et al. 2007; Ma et al. 2007; Baldomir et al. 2007; Franco et al. 2007; škorvánek et al. 2007; Poddar et al. 2007; Biswas et al. 2008; Franco et al. 2008; Gorsse et al. 2008; Li 2008; Gass et al. 2008; Lu et al. 2008; Santanna et al. 2008; Serantes et al. 2008; Pekała and Drozd 2008; Juan and Gui 2009; Gorria et al. 2009; Phan et al. 2009; Babita et al. 2009; Calderon-Ortiz et al. 2009; Das et al. 2009; Phan et al. 2010; Burianova et al. 2010; Nelson et al. 2002). However, up to now, not much effort has been devoted to the rare earth bulk nanocrystalline metals.

As the only simple ferromagnet among the rare earth elements at room temperature, the metal gadolinium (Gd) has been broadly investigated in past decades (Geldart et al. 1962; Legvold 1980; Gschneidner and Pecharsky

2000; Dan'kov et al. 1998) and has drawn tremendous attention, particularly with respect to the finite-temperature magnetic properties and magnetocaloric effect. It is well known that Gd crystallizes in the hexagonal close-packed structure with a lattice constant of $a = 3.629$ Å, $c/a = 1.579$. The magnetic phase transition from paramagnet to ferromagnet is second-order transformation taking place at the Curie temperature around 293 K, close to room temperature.

In our recent research, a novel technique has been developed for preparing full dense bulk size-controllable nanocrystalline pure rare earth metals (Song et al. 2006), which enabled us to study the remarkable influence of nanostructure on the all kinds of properties of the rare earth metal Gd. However, the magnetocaloric properties of bulk nanocrystalline Gd metals remain unexplored for the moment. In the present work, therefore, it is the aim of this study to investigate the effect of nanostucture, as represented in the bulk nanocrystalline Gd metals, on the magnetic entropy change of Gd.

Experimental

The experimental details on the preparation and characterization of the consolidated bulk of the pure rare earth Gd metals have been published elsewhere (Zeng et al. 2009).

The initially prepared Gd nanoparticles, prepared by the inert-gas condensation method, were consolidated using by Spark Plasma Sintering. The sintering conditions are as follows: vacuum, temperature in the range 250–700°C with a heating rate of 50°C min^{-1}, pressure 500 MPa and without heat preservation time. After sintering, the consolidated bulk nanocrystalline metals cooled down to room temperature.

The microstructures of the consolidated bulk of the pure rare earth Gd metals were observed with transmission electron microscopes and select area electron diffraction. It is revealed from the TEM micrograph observation that the average grain sizes in the as-consolidated bulk at 280 and 700°C, and the coarse-grained polycrystalline Gd raw material, are 15, 100 and 1,000 nm, respectively.

The magnetic properties of the as-consolidated bulk as well as the coarse-grain specimens were measured by using a Physics Property Measurement System (PPMS, Quantum Design).

The magnetic entropy of a magnetic system can be derived from the Maxwell equation (1):

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \tag{1}$$

In an isothermal magnetization process, the magnetic entropy change (ΔS_M) can be derived from Eq. 1 by integrating from the initial field 0 to the final field H, as following shown:

$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T}\right) dH \tag{2}$$

where the symbols S, M, H, and T represent the magnetic entropy, the magnetization of material, the applied magnetic field and the temperature of the system, respectively.

In the case of measurements of the magnetization made at a certain constant temperature, and at discrete intervals of H, the above Maxwell expression can be numerically approximated with the following expression (3):

$$\Delta S_M\left(\frac{T_1+T_2}{2}\right) = \frac{1}{T_2-T_1}\int_0^H [M(T_2,H)-M(T_1,H)]dH = \sum \frac{M(T_2,H)-M(T_1,H)}{T_2-T_1}\Delta H \tag{3}$$

where M (T_1, H) and M (T_2, H) represent the values of the magnetization in a magnetic field H at the temperatures T_1 and T_2.

Results and discussion

Figure 1 displays the ZFC magnetization curves of the bulk Gd metals at temperature range from 3 to 335 K in the applied magnetic field of 100 Oe. The values of the Curie temperatures (T_C) have been obtained from the inflection point of the magnetization data at low field. Thus, the magnetic orderings, respectively, at 296.2, 289 and 294.2 K, determined from the magnetization of the samples as a function of temperature, are associated with the second-order paramagnetic to ferromagnetic transition. It can be well found that the Curie temperature of the bulk Gd metals decreases as the grain size decrease, from the 296.2 K of coarse-grained polycrystalline Gd down to 289 K of the consolidated bulk nanocrystalline Gd at 280°C. In other words, the Curie temperature T_C of the nanocrystalline Gd shifts by more than 7 K below that of coarse-grained Gd sample. Such behavior has been observed for other systems, e.g. for FePt (Rellinghaus et al. 2003) nanopaticles. Meanwhile, the curves of the consolidated bulks exhibit broader shape near the Curie temperature compared with the coarse-grained Gd.

Correspondingly, the magnetizations of the samples at 3 K are 3.1, 2.7 and 2.1 emu/g, respectively, determined also from the figure. This value also decreases with the decrease in grain size.

The magnetization behaviors at 5 K of the consolidated bulk of the pure rare earth metals as well as the

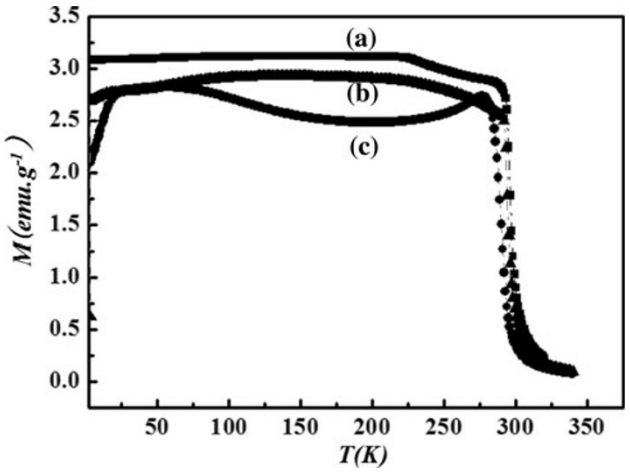

Fig. 1 *M–T* curves of the rare earth Gd metals with different grain size: **a** raw material, **b** the as-consolidated at 700°C and **c** the as-consolidated at 280°C

coarse-grained polycrystalline Gd metal measured in the magnetic field from 0 to 5.0 T are shown in Fig. 2a–c. It is well seen that, the saturation magnetization rises from 223.97 emu/g of the consolidated bulk at 280°C to 250.36 emu/g of the consolidated bulk at 700°C, and to 278.97 emu/g of the coarse-grained polycrystalline Gd metal. However, comparing it with the coarse-grained bulk Gd, the magnetizations decrease by about 20 and 10% for the as-consolidated samples, respectively, exhibiting a distinct depressed magnetization in the bulk nanocrystalline Gd metals.

In order to well understand the effect of grain sizes on magnetic entropy change (ΔS_M) in the bulk Gd metals, the isothermal magnetization measurements have been carried out up to a maximum magnetic field of 5 T at different temperatures in the vicinity of T_C. The magnetization

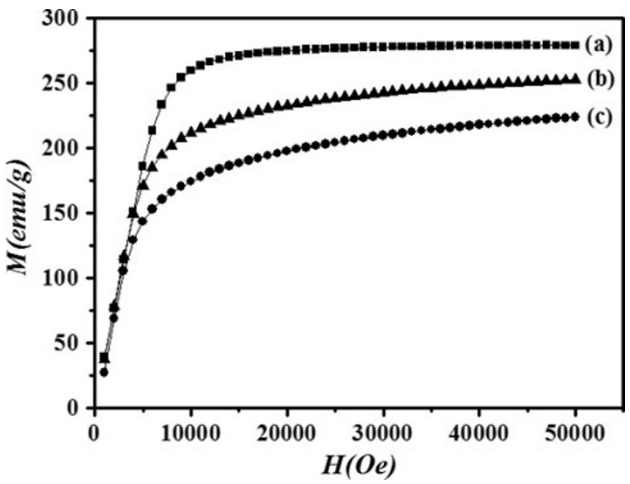

Fig. 2 *M–H* curves of the rare earth Gd metals with different grain size under 5 K: **a** raw material, **b** the as-consolidated at 700°C and **c** the as-consolidated at 280°C

behaviors of the consolidated bulk of the pure rare earth metals measured between 270 and 310 K in the magnetic field from 0 to 5.0 T are shown in Fig. 3a–c. The magnetization isotherms of both the consolidated bulk metals show the typical magnetic order transition from ferromagnetic to paramagnetic state, which is the characteristic

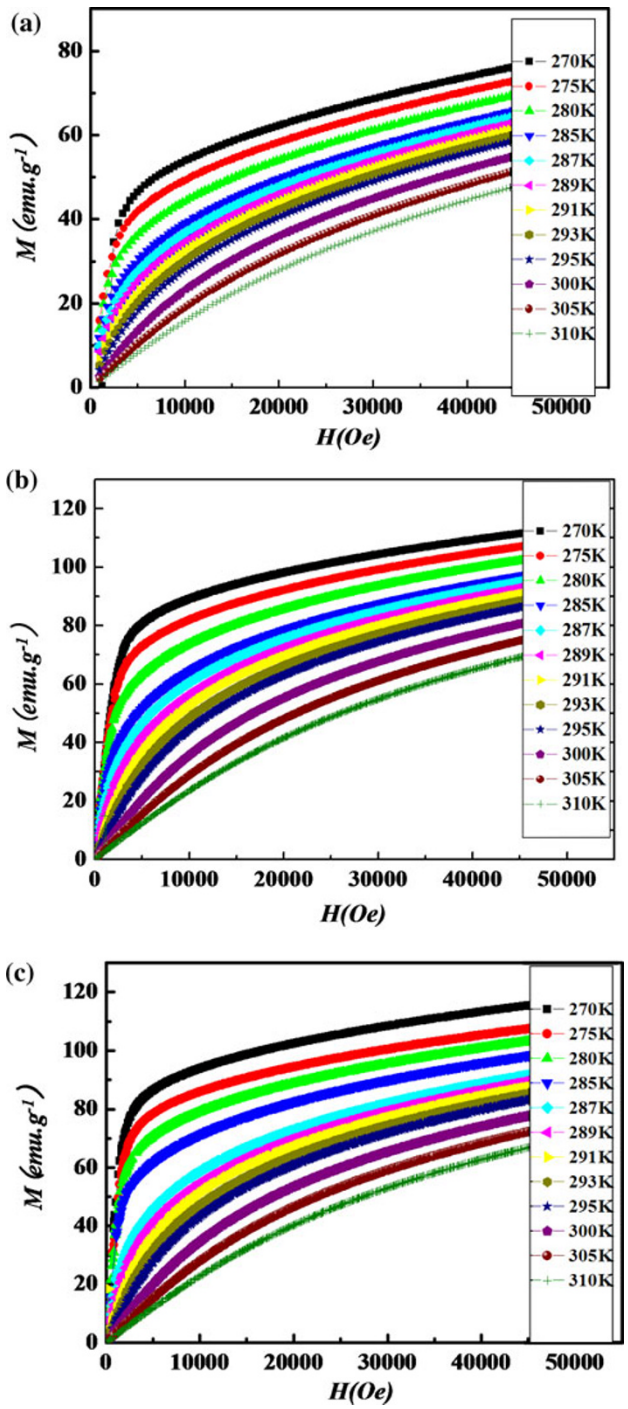

Fig. 3 Magnetization isotherms of the rare earth Gd metals with different grain size under 5 K: **a** the as-consolidated at 280°C, **b** the as-consolidated at 700°C and **c** raw material

of the second-order magnetic-crystallographic transition induced by the strong variation of temperature under magnetic field around the Curie temperature.

The nature of the magnetic phase transition in the Gd metals has been examined by using Banerjee criterion (Banerjee 1964). According to which the slope of M^2 versus H/M curves (Arrott plot) denotes whether the observed magnetic phase transition is of the first order (negative slope) or, second order (positive slope). The so-called Arrott plots of H/M versus M^2 near the magnetic transition temperature were performed for a temperature interval between 270 and 310 K, as shown in Fig. 4a–c. All the H/M versus M^2 curves exhibit the positive slope indicating that the transitions between the ferromagnetic and paramagnetic phases in all samples are of the second-order transition (SOMT). As we know that the paramagnetic-ferromagnetic phase transition in polycrystalline Gd is the second-order magnetic transition. In other words, the nanosturctures do not change the magnetic transition and still preserve the second-order ferromagnetic → paramagnetic magnetic phase transition in the bulk nanocrystalline Gd metals.

The temperature dependence of magnetic entropy change (ΔS_M) value for all, upon the magnetic applied field changes of 5 T, determined numerically using Eq. 3 and the corresponding magnetization (M) curves in Fig. 3, displaying a maximum negative value around the Curie temperature, is shown in Fig. 5.

Figure 5 shows the temperature dependencies of the ΔS curves for the as-consolidated and coarse-grained bulk Gd metals measured directly from 270 to 310 K in a magnetic field from 0 to 5 T. It is well known that the MCE peaks at the appropriate magnetic phase-transition temperature of the magnetic material. The maximum of the ΔS peaks at its Curie temperature (T_C). MCE shows that the ΔS peak temperatures of the as-consolidated at 280°C and at 700°C as well as coarse-grained bulk Gd samples are 288, 290, and 294 K, respectively, which are slightly smaller than the values determined from the ZFC measurement; the corresponding peak values of ΔS of the three bulk samples are 4.47 K, 7.73 K, and 10.07 J kg^{-1} K^{-1}, respectively. Obviously, the ΔS values of the bulk nanocrystalline Gd metals are far lower than that of the corresponding coarse-grained bulk Gd. Remarkably, the peak value in the as-consolidated at 280°C (4.47 J kg^{-1} K^{-1}) is nearly 2 times smaller than in coarse-grained bulk Gd (10.07 J kg^{-1} K^{-1}). Thus, it indicates that the grain sizes can affect the magnetocaloric effect in the Gd metals.

The decreasing of the crystallite size in the nanostructural Gd samples leads to a reduction of the maximum value for the ΔS, specially the value only attaining to 4.47 J kg^{-1} K^{-1} for the SPS 280°C sample. The ΔS peak temperatures have also been found to be strongly dependent on

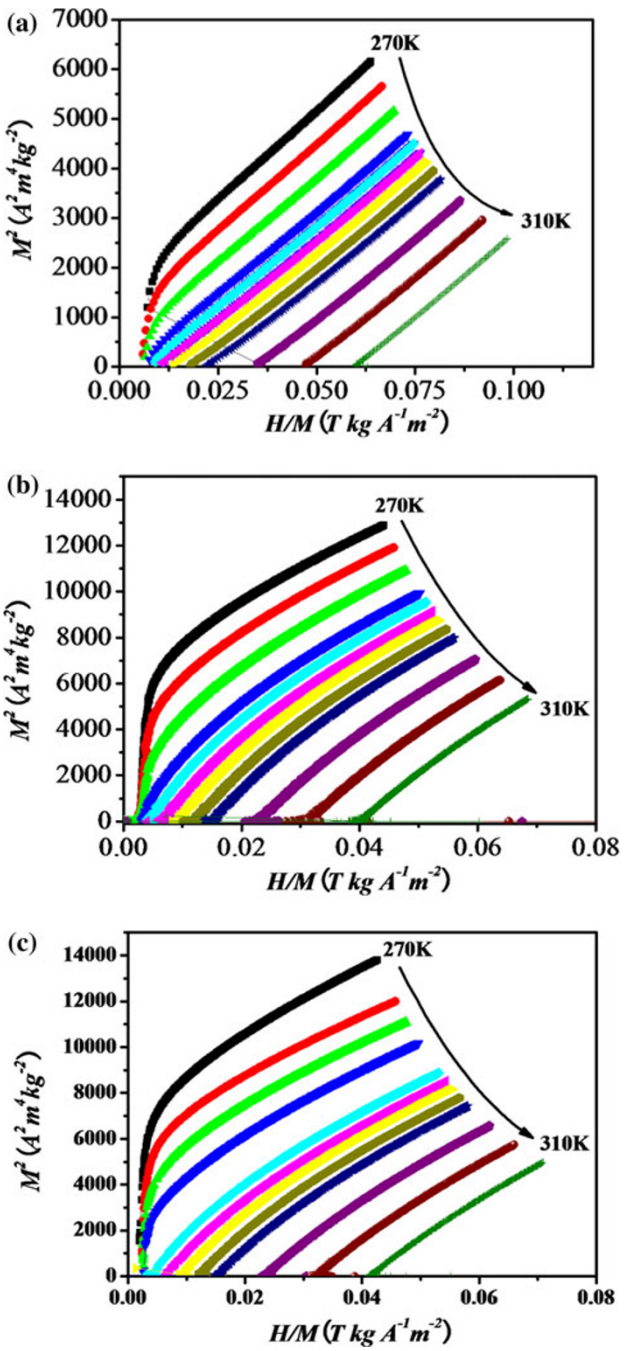

Fig. 4 Arrott plots of the nanocrystalline bulk Gd metals around the Curie temperature: **a** the as-consolidated at 280°C, **b** the as-consolidated at 700°C and **c** raw material

the crystallite size of the bulk Gd materials and turned out to be reduced to 6 K compared with the coarse-grained bulk Gd. The broadening of ΔS peaks revealed in the as-consolidated samples in comparison with the coarse-grained bulk Gd metal, can be at least partially, attributed to the structural disorder due to the significantly increased total grain boundary volume. It is well seen in the TEM, especially the HRTEM (Zeng et al. 2009), that the grain

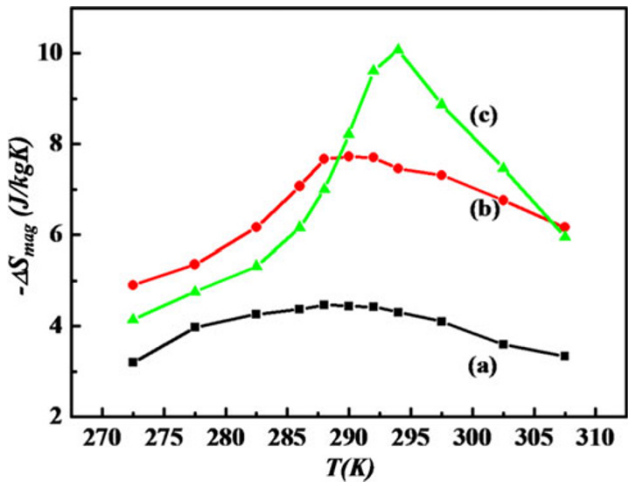

Fig. 5 The magnetic entropy changes (ΔS) of the bulk Gd samples: **a** the as-consolidated at 280°C, **b** the as-consolidated at 700°C and **c** raw material

boundary microstructure in the nanocrystalline Gd is like the disordered amorphous phase state, being very different from that in the crystal grain. The amount of disordered phase in the bulk nanocrystalline Gd is more than that in the coarse-grained Gd due to the significantly increased total grain boundary volume. It is well known that the ferromagnetic ordering in Gd depends on the Ruderman-Kittel-Kasuya-Yosida interaction, which is sensitive to the atomic distances. Therefore, it is expected that the exchange interaction at the grain boundary would be different from that at the internal region of the grain. Consequently, the reduction in the magnetocaloric effect of the bulk nanocrystalline Gd metals can be partly ascribed to the existence of large amount of disordered amorphous phase (grain boundaries). On the other hand, the magnetocaloric effect is related to the magnetic moment, however, the reduction of magnetic moment due to grain size reduction, which causes the decrease in magnetocaloric effect for the bulk nanocrystalline Gd metals.

In practice, the refrigerant capacity (Q), how much heat can be transferred between the cold and hot sinks in one ideal refrigeration cycle, is also an important parameter for selecting potential substances as magnetic refrigerants. The larger the Q is, the better the magnetocaloric material is. According to the method reported in the previous literature (Pecharsky and Gschneidner 2001), the Q is defined as

$$Q = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S_{\text{M}} dT \tag{4}$$

where T_{cold} and T_{hot} are the temperature of the cold and hot sinks, respectively.

In order to get better comparison, the related magnetocaloric parameters of the coarse-grained and consolidated bulk Gd metals at 5 T are listed in the Table 1. Table 1 shows the comparison of magnetic entropy changes (ΔS), MCE peak temperatures (T_{P}), relative cooling power (RCP), Curie temperatures (T_{C}) determined from the ZFC measurement and grain size (D) between coarse-grained sample and bulk nanocrystalline Gd metals.

Table 1 The magnetic entropy changes (ΔS), MCE peak temperatures (T_{P}), relative cooling power (RCP), Curie temperatures (T_{C}) and grain size (D) for the bulk Gd metals

	Raw material	SPS 280°C metal	SPS 700°C metal
ΔS (J kg^{-1} K^{-1})	10.07	4.47	7.73
T_{P} (K)	294	288	290
T_{C} (K)	296.2	289	294.2
RCP (J kg^{-1})	240	140	234
D (nm)	1,000	15	100

Finally, it is worth to note that the maximum value for the magnetocaloric effect decreases around 56 and 33%, respectively, for the SPS 280°C sample and the SPS 700°C sample in comparison with the coarse-grained bulk Gd. However, the magnetic entropy change peaks of the bulk nanocrystalline Gd metals are broaden and showing more constant than the coarse-grained bulk Gd in the same temperature span, which suggested that the bulk nanocrystalline could cover a large working temperature span. This large temperature interval with almost constant value of ΔS could be interesting for magnetic refrigeration applications at room temperature.

These results reveal that grain size can remarkably affect the MCE in the Gd metals and consequently stongly influence the conversion performance in the AMR. Therefore, our present work about the grain sizes on magnetocaloric effect may open an important field for the magnetic refrigeration practice applications.

Conclusions

In conclusion, the bulk nanocrystalline Gd matels have been consolidated from Gd nanoparticles using spark plasma sintering (SPS) technique. At 280°C, the mean size of the sintered Gd sample is 15 nm, and it increases to 100 nm when the temperature rises to 700°C. However, the Curie temperatures T_{C} of Gd metals are, respectively, at 296.2, 289 and 294.2 K, shifted by more than 7 K below that of coarse-grained polycrystalline Gd. Meanwhile, the nanosturctures do not change the magnetic transition and the second- order magnetic transitions still remain. Magnetic entropy changes (ΔS) show that with the decrease of Gd grains from micrometer to nanometer, the ΔS drops surprising from 10.07 to 4.47 J kg^{-1} K^{-1}, and their

resultant ΔS uniformly peaks at 294, 290, and 288 K, respectively. All results imply the remarkable influence of the nanostructure on the magnetocaloric effects of Gd due to the finite size effect and grain boundaries.

In addition, it is worth to note that the magnetic entropy change peaks of the bulk nanocrystalline Gd metals are broaden and showing more constant than the coarse-grained counterpart in the same temperature span, which suggested that the bulk nanocrystalline metals could cover a large working temperature span. This large temperature interval with almost constant value of ΔS could be interesting for magnetic refrigeration applications at room temperature.

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